# Ionic solutions under high pressures II : pressure and temperature effects on the dissociation of the Co(NH3)6 3+ ・SO4 2- ion-pair

AUTHOR(S):

Nakahara, Masaru; Shimizu, Kiyoshi; Osugi, Jiro

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# IONIC SOLUTIONS UNDER HIGH PRESSURES II

## Pressure and Temperature Effects on the Dissociation of the $Co(NH_3)_6^{3+} \cdot SO_4^{2-}$ Ion-Pair

BY MASARU NAKAHARA, KIYOSHI SHIMIZU AND JIRO OSUGI

The dissociation constant of the $Co(NH_3)_6^{3+} \cdot SO_4^{2-}$ ion-pair in water has been determined at high pressures up to 5,000 atm at the temperatures of 15°, 25° and 40°C, using the previous electrochemical data[1]. Then the closest approach distances of the ion-pair, $d_{D\text{-}R}$, $d_F$ and $d_B$, were calculated from the theoretical equations of Denison-Ramsey[2], Fuoss[3] and Bjerrum[4], respectively. All of them decrease almost linearly with increasing pressure. This decrease in $d$'s with pressure could be understood, considering that these ion-pairs are solvent-separated ones in which both cations and anions are already extensively solvated in the loosely associated state. And this decrease in $d$ turns out to be the reason why there appears a plateau in the curve of log $K$ *vs* pressure above 2,500 atm. Therefore, it would be concluded that pressure affects not only upon the solvation energies of the free ions through the dielectric constant of the solvent but also upon the Coulombic interaction energies between the cations and the anions in the ion-pairs through the closest-approach distance.

### Introduction

Pressure and temperature effects on the dissociation constants of various weak acids and bases in water have been studied and interpreted in terms of the change in the dielectric constants of solvents[5][6]. But the dissociation constants of ion-pairs have not yet been investigated sufficiently at high pressures; most of them increase with pressure, but some of them decrease[7] or remain constant[7]. In aqueous solutions at high pressures, the dissociation constants have been determined for $Mg^{2+} \cdot$

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2) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955)
3) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958)
4) N. Bjerrum, *Kgl. Danske Videnskab Selskab.*, 7, No. 9 (1926)
5) S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, Chap. 7. ed. by R.S. Bradley, Academic Press (1963)
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$SO_4^{2-}$ [8], $Co(NH_3)_6^{3+}\cdot Cl^-$ [9], $Fe^{3+}\cdot NO_3^-$ [10], $Fe^{3+}\cdot Cl^-$ [10], $La^{3+}\cdot Fe(CN)_6^{3-}$ [11], $Mn^{2+}\cdot SO_4^{2-}$ [12], $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$ [13] and $La^{3+}\cdot SO_4^{2-}$ [14]. In this paper the dissociation constant of the $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$-ion-pair in water has been re-examined extensively up to the higher pressure (~5,000 atm) than in the previous paper[1] and analyzed with the aid of theoretical equations for the dissociation constant of the ion-pair in order to obtain some informations about the molecular structure of the ion-pair in water at high pressures.

## Calculations and Considerations

In the aqueous solution of $[Co(NH_3)_6]_2(SO_4)_3$, the first ionization may be assumed complete, and then ion-pair, $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$ would be in equilibrium with their free ions, $Co(NH_3)_6^{3+}$ and $SO_4^{2-}$:

$$\underset{m}{[Co(NH_3)_6]_2(SO_4)_3} \longrightarrow \underset{2m}{2\ Co(NH_3)_6^{3-}\cdot SO_4^{2-}} + \underset{m}{SO_4^{2-}}, \quad (1)$$

$$\underset{2m(1-\alpha)\ (m_1)}{Co(NH_3)_6^{3+}\cdot SO_4^{2-}} \rightleftharpoons \underset{2m\alpha\ (m_3)}{Co(NH_3)_6^{3+}} + \underset{2m\alpha+m\ (m_2)}{SO_4^{2-}}, \quad (2)$$

where $m$ is the stoichiometric molar concentration and $\alpha$ is the degree of the dissociation of the ion-pair. Then, the dissociation constant $K$ corresponding to eq. (2) is defined as follows:

$$K = \frac{m_3 m_2}{m_1}\cdot\frac{f_3 f_2}{f_1},$$

$$= \frac{\alpha(1+2\alpha)m}{1-\alpha}\cdot\frac{f_3 f_2}{f_1}, \quad (3)$$

where $m_3$, $m_2$ and $m_1$ are the molar concentrations of $Co(NH_3)_6^{3+}$, $SO_4^{2-}$ and $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$, and $f_3$, $f_2$ and $f_1$ are the activity coefficients of respective ions. Activity coefficients are calculated from the Debye-Hückel limiting equation,

$$-\log f_i = 1.291 \times 10^{-6}\cdot z_i^2\cdot \Gamma^{1/2}/(DT)^{3/2} \equiv z_i^2 y, \quad (4)$$

where $z_i$, $D$ and $\Gamma$ are the ionic valence of $i$-ion, the dielectric constant of water and the ional concentration (=2 × ionic strength), respectively. In this system, the ional concentration,

$$\Gamma = \Sigma m_i z_i^2 = 6m(4\alpha+1). \quad (5)$$

From eqs. (3) and (4), we have

$$\log K = \{\log\alpha + \log(1+2\alpha) - \log(1-\alpha)\} + \log m - 12y, \quad (6)$$

which is a function only of $\alpha$, because $y$ is also known from $\alpha$ according to eqs. (4) and (5). This unknown variable $\alpha$ is to be determined from the solution of the conductance equation of this ionic

8) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962)
9) K. Shimizu, H. Takizawa and J. Osugi, *This Journal*, **23**, 1 (1963)
10) R. A. Horne, B. R. Meyers and G. R. Frysinger, *Inorg. Chem.*, **3**, 452 (1964)
11) S. D. Hamann, P. J. Pearce and W. Strauss, *J. Phys. Chem.*, **68**, 375 (1964)
12) F. H. Fisher and D. F. Davis, *ibid.*, **69**, 2595 (1965)
13) J. Osugi, K. Shimizu and H. Takizawa, *This Journal*, **36**, 1 (1966)
14) F. H. Fisher and D. F. Davis, *J. Phys. Chem.*, **71**, 819 (1967)

system, using the theoretical equation of Onsager[15] in the following way. Now, the solvent-corrected specific conductance of this system,

$$\kappa' = \Sigma |z_i| (m_i/10^3) \cdot \lambda_i \qquad (i = 3,2,1). \tag{7}$$

And from definition

$$\kappa' = \Lambda \cdot (10^{-3} C) \qquad (C = 6m). \tag{8}$$

Inserting $\kappa'$ in eq. (8) and $m_i$ in eq. (2) into eq. (1), we have

$$\Lambda = \alpha(\lambda_3 + \lambda_2) + \frac{1-\alpha}{3}(\lambda_1 + \lambda_2). \tag{9}$$

Here, for $\lambda_i$ Onsager's equation is assumed;

$$\lambda_i = \lambda^\circ_i - S_i(\lambda^\circ_i, D, \eta^\circ, T) \cdot \sqrt{C} \cdot \sqrt{4\alpha+1} \qquad (i = 3, 2), \tag{10}$$

where $S_i$ is a constant which is determined by the dielectric constant, $D$ (Table 1), the viscosity $\eta^\circ$ (Table 2) of solvent water, temperature $T$ and the limiting equivalent conductance, $\lambda^\circ_i$, of $i$-ion. And, furthermore, for the equivalent conductance of the $Co(NH_3)_6^{3+} \cdot SO_4^{2-}$ ion-pair, it was assumed[16] that

$$\lambda_1 = \lambda_3 / 3. \tag{11}$$

Inserting eqs. (10) and (11) into eq. (9), we can get finally,

$$\Lambda = \alpha\{\lambda^\circ_3 + \lambda^\circ_2 - (S_3 + S_2) \cdot \sqrt{C} \cdot \sqrt{4\alpha+1}\} + \frac{1-\alpha}{3}\{\lambda^\circ_3/3 + \lambda^\circ_2 - (S_3/3 + S_2) \cdot \sqrt{C} \cdot \sqrt{4\alpha+1}\}. \tag{12}$$

$\alpha$ in this equation is able to be solved by means of successive approximation. Then, the obtained values of $\alpha$ are put into eqs. (5), (4) and (6), so that the values of log $K$ may be obtained, which are tabulated in Tables 3 (a), (b) and (c) with their average values.

Table 1 The dielectric constant of water at high pressures, $D^{(P)}$‡

| $T$, °C / $P$, atm | 15 | 25 | | 40 |
|---|---|---|---|---|
| | | (Fisher)* | | |
| 1 | 82.23 | 78.36 | 78.58 | 73.35 |
| 500 | 84.62 | 80.55 | 80.81 | 75.38 |
| 1,000 | 86.80 | 83.06 | 82.88 | 77.22 |
| 1,500 | 88.83 | 84.55 | 84.80 | 78.94 |
| 2,000 | 90.69 | 86.20 | 86.57 | 80.55 |
| 2,500 | 92.46 | 87.84 | | 82.05 |
| 3,000 | 94.11 | 89.41 | | 83.47 |
| 3,500 | 95.69 | 90.90 | | 84.83 |
| 4,000 | 97.20 | 92.31 | | 86.12 |
| 4,500 | 98.64 | 93.64 | | 87.37 |
| 5,000 | 100.04 | 94.89 | | 88.55 |

‡ calculated from the Owen-Brinkley equation[15]; $1 - D^{(1)}/D^{(P)} = AD^{(1)} \log(B+P)/(B+1)$

* F. H. Fisher's calculations: Ref. 8)

15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold (1959)

16) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 168

Table 2 The viscosity coefficient of water at high pressures, $\eta^{\circ(P)}$‡ (cp)

| $T$, °C / $P$, atm | 15 | 25 | | 40 |
|---|---|---|---|---|
| | | | (Fisher)* | |
| 1 | 1.156 | 0.8937 | 0.8937 | 0657 |
| 500 | 1.129 | 0.8865 | 0.9014 | 0.663 |
| 1,000 | 1.122 | 0.8905 | 0.9132 | 0.676 |
| 1,500 | 1.135 | 0.9053 | 0.9314 | 0.695 |
| 2,000 | 1.158 | 0.9266 | 0.9604 | 0.715 |
| 2,500 | 1.190 | 0.9534 | | 0.737 |
| 3,000 | 1.230 | 0.9709 | | 0.761 |
| 3,500 | 1.276 | 1.0022 | | 0.788 |
| 4,000 | 1.328 | 1.0392 | | 0.817 |
| 4,500 | 1.385 | 1.0756 | | 0.846 |
| 5,000 | 1.448 | 1.1163 | | 0.880 |

‡ from the data of J. B. Cappi[17]

* P. W. Bridgman's data used by F. H. Fisher[8]

Figs. 1 and 2 show the relations between the average values of log $K$ and pressure and temperature, respectively. From these plots, the following thermodynamic parameters concerned with the dissociation of the ion-pair are calculated from the thermodynamic relations,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta\bar{V}^\circ}{RT}\ , \tag{13}$$

$$\left(\frac{\partial \ln K}{\partial (1/T)}\right)_P = -\frac{\Delta\bar{H}^\circ}{R}\ , \tag{14}$$

$$\Delta\bar{S}^\circ = \frac{\Delta\bar{H}^\circ - \Delta\bar{G}^\circ}{T}\ , \tag{15}$$

where

$$\Delta\bar{G}^\circ = -RT\ln K\ . \tag{16}$$

The derived thermodynamic parameters, $\Delta\bar{V}^\circ$, $\Delta\bar{H}^\circ$, $\Delta\bar{G}^\circ$ and $\Delta\bar{S}^\circ$ are given in Table 4.

As shown in Fig. 1, the curves of log $K$ *vs* pressure show almost linear increase up to 2,500 atm and then a plateau, and again increase near 5,000 atm (at 40°C, log $K$ seems to be too low above 3,500 atm). The dissociation constants of other 2–2, 3–2 and 3–3 ion-pairs are shown up to 2,000 atm in the same figure, and they appear to have the same inclination at higher pressures as in the case of the $Co(NH_3)_6^{3+}\cdot SO_4^{2-}$ ion-pair. As stated by Hamann[5)6)], increase in ionization of electrolytes by pressure would be due to the increase in solvation energies of free ions, but the plateau appeared above 2,500 atm could not be explained only from this point of view because of the gradual increase in the dielectric constant of solvent without any occurrence of the dielectric saturation in the bulk sense. As discussed later in detail, the loosely associated ion-pairs, which are not so rigid as weak acid or base molecules, would suffer significant effects of pressure on their molecular state, probably until they have been compressed to be tight. These ion-pairs would be considered to be solvent-separated

17) J.B. Cappi, Ph.D. Thesis, London University (1964)

ones[18], because the absolute value of $\Delta\bar{V}^\circ$ of this ion-pair is not so large as that expected from the electrostriction even at normal pressure[5]. And in the case of this ion-pair, Hepler's correlation[19] between $\Delta\bar{S}^\circ$ and $\Delta\bar{V}^\circ$ was not obtained.

Table 3(a) log $K$ at 15°C

| Sample# / $P$, atm | A | B | C | D | E | Average* |
|---|---|---|---|---|---|---|
| 1 | $\bar{4}$.328 | $\bar{4}$.342 | $\bar{4}$.345 | $\bar{4}$.336 | $\bar{4}$.323 | $\bar{4}$.335 |
| 500 | $\bar{4}$.399 | $\bar{4}$.416 | $\bar{4}$.426 | $\bar{4}$.416 | $\bar{4}$.413 | $\bar{4}$.414 |
| 1,000 | $\bar{4}$.459 | $\bar{4}$.489 | $\bar{4}$.495 | $\bar{4}$.500 | $\bar{4}$.488 | $\bar{4}$.486 |
| 1,500 | $\bar{4}$.525 | $\bar{4}$.546 | $\bar{4}$.564 | $\bar{4}$.564 | $\bar{4}$.561 | $\bar{4}$.552 |
| 2,000 | $\bar{4}$.595 | $\bar{4}$.603 | $\bar{4}$.641 | $\bar{4}$.649 | $\bar{4}$.650 | $\bar{4}$.650 |
| 2,500 | $\bar{4}$.630 | $\bar{4}$.636 | $\bar{4}$.655 | $\bar{4}$.661 | $\bar{4}$.664 | $\bar{4}$.649 |
| 3,000 | $\bar{4}$.639 | $\bar{4}$.668 | $\bar{4}$.685 | $\bar{4}$.696 | $\bar{4}$.700 | $\bar{4}$.678 |
| 3,500 | $\bar{4}$.629 | $\bar{4}$.656 | $\bar{4}$.707 | $\bar{4}$.683 | $\bar{4}$.687 | $\bar{4}$.672 |
| 4,000 | $\bar{4}$.636 | $\bar{4}$.662 | $\bar{4}$.688 | $\bar{4}$.689 | $\bar{4}$.695 | $\bar{4}$.674 |
| 4,500 | $\bar{4}$.654 | $\bar{4}$.686 | $\bar{4}$.697 | $\bar{4}$.688 | $\bar{4}$.692 | $\bar{4}$.683 |
| 5,000 | $\bar{4}$.687 | $\bar{4}$.706 | $\bar{4}$.731 | $\bar{4}$.745 | $\bar{4}$.745 | $\bar{4}$.723 |

# A: $1.761\times10^{-4}$N, B: $2.317\times10^{-4}$N, C: $3.243\times10^{-4}$N, D: $3.984\times10^{-4}$N, E: $4.633\times10^{-4}$N at 1 atm

* $(\log K)_{\text{average}} = [(\log K)_A+(\log K)_B+(\log K)_C+(\log K)_D+(\log K)_E]/5$

Table 3(b) log $K$ at 25°C

| Sample# / $P$, atm | A | B | C | D | E | Average |
|---|---|---|---|---|---|---|
| 1 | $\bar{4}$.319 | $\bar{4}$.331 | $\bar{4}$.332 | $\bar{4}$.318 | $\bar{4}$.301 | $\bar{4}$.320 |
| 500 | $\bar{4}$.369 | $\bar{4}$.374 | $\bar{4}$.384 | $\bar{4}$.375 | $\bar{4}$.369 | $\bar{4}$.374 |
| 1,000 | $\bar{4}$.410 | $\bar{4}$.422 | $\bar{4}$.428 | $\bar{4}$.425 | $\bar{4}$.419 | $\bar{4}$.421 |
| 1,500 | $\bar{4}$.461 | $\bar{4}$.483 | $\bar{4}$.496 | $\bar{4}$.484 | $\bar{4}$.486 | $\bar{4}$.482 |
| 2,000 | $\bar{4}$.492 | $\bar{4}$.510 | $\bar{4}$.522 | $\bar{4}$.526 | $\bar{4}$.521 | $\bar{4}$.514 |
| 2,500 | $\bar{4}$.523 | $\bar{4}$.542 | $\bar{4}$.557 | $\bar{4}$.556 | $\bar{4}$.554 | $\bar{4}$.546 |
| 3,000 | $\bar{4}$.555 | $\bar{4}$.573 | $\bar{4}$.587 | $\bar{4}$.592 | $\bar{4}$.588 | $\bar{4}$.579 |
| 3,500 | $\bar{4}$.565 | $\bar{4}$.590 | $\bar{4}$.603 | $\bar{4}$.606 | $\bar{4}$.609 | $\bar{4}$.595 |
| 4,000 | $\bar{4}$.572 | $\bar{4}$.591 | $\bar{4}$.611 | $\bar{4}$.612 | $\bar{4}$.610 | $\bar{4}$.599 |
| 4,500 | $\bar{4}$.590 | $\bar{4}$.613 | $\bar{4}$.635 | $\bar{4}$.643 | $\bar{4}$.649 | $\bar{4}$.626 |
| 5,000 | $\bar{4}$.609 | $\bar{4}$.632 | $\bar{4}$.648 | $\bar{4}$.657 | $\bar{4}$.657 | $\bar{4}$.640 |

# A: $1.761\times10^{-4}$N, B: $2.317\times10^{-4}$N, C: $3.243\times10^{-4}$N, D: $3.984\times10^{-4}$N, E: $4.633\times10^{-4}$N at 1 atm

18) T. R. Griffiths and M. C. R. Symons, *Mol. Phys.*, 3, 90 (1960)
19) L. G. Hepler, *J. Phys. Chem.*, 69, 965 (1965)

Table 3(c) log $K$ at 40°C

| $P$, atm \ Sample# | A | B | C | D | E | Average |
|---|---|---|---|---|---|---|
| 1 | $\bar{4}$.316 | $\bar{4}$.315 | $\bar{4}$.328 | $\bar{4}$.312 | $\bar{4}$.302 | $\bar{4}$.315 |
| 500 | $\bar{4}$.349 | $\bar{4}$.349 | $\bar{4}$.366 | $\bar{4}$.349 | $\bar{4}$.340 | $\bar{4}$.351 |
| 1,000 | $\bar{4}$.374 | $\bar{4}$.392 | $\bar{4}$.388 | $\bar{4}$.389 | $\bar{4}$.378 | $\bar{4}$.384 |
| 1,500 | $\bar{4}$.409 | $\bar{4}$.433 | $\bar{4}$.441 | $\bar{4}$.439 | $\bar{4}$.428 | $\bar{4}$.430 |
| 2,000 | $\bar{4}$.452 | $\bar{4}$.470 | $\bar{4}$.473 | $\bar{4}$.478 | $\bar{4}$.465 | $\bar{4}$.467 |
| 2,500 | $\bar{4}$.469 | $\bar{4}$.482 | $\bar{4}$.490 | $\bar{4}$.491 | $\bar{4}$.488 | $\bar{4}$.484 |
| 3,000 | $\bar{4}$.480 | $\bar{4}$.490 | $\bar{4}$.503 | $\bar{4}$.502 | $\bar{4}$.493 | $\bar{3}$.493 |
| 3,500 | $\bar{4}$.469 | $\bar{4}$.489 | $\bar{4}$.501 | $\bar{4}$.494 | $\bar{4}$.489 | $\bar{4}$.488 |
| 4,000 | $\bar{4}$.426 | $\bar{4}$.481 | $\bar{4}$.489 | $\bar{4}$.487 | $\bar{4}$.478 | $\bar{4}$.479 |
| 4,500 | $\bar{4}$.451 | $\bar{4}$.474 | $\bar{4}$.487 | $\bar{4}$.474 | $\bar{4}$.474 | $\bar{4}$.472 |
| 5,000 | $\bar{4}$.392 | $\bar{4}$.450 | $\bar{4}$.460 | $\bar{4}$.456 | $\bar{4}$.451 | $\bar{4}$.452 |

# A: $1.756\times10^{-4}$N, B: $2.310\times10^{-4}$N, C: $3.233\times10^{-4}$N, D: $3.972\times10^{-4}$N, E: $4.619\times10^{-4}$N at 1 atm

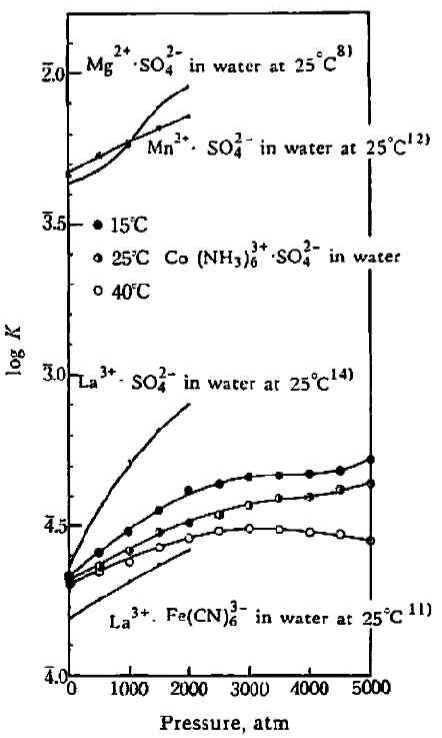


Fig. 1 log $K$ *vs* pressure

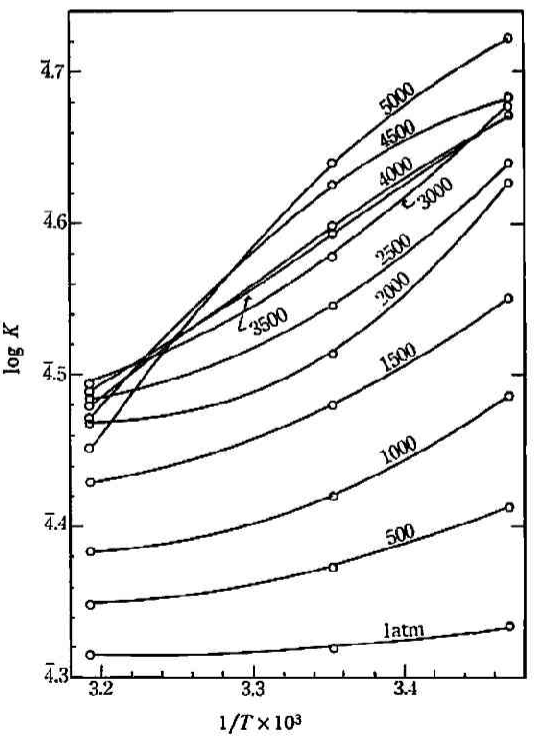


Fig. 2 log $K$ *vs* $1/T$

Table 4 Thermodynamic parameters concerned with the dissociation of the ion-pair

| Thermodynamic parameters / $P$, atm | $\Delta\bar{G}^\circ$ (kcal/mole) 25°C | $\Delta\bar{H}^\circ$ (kcal/mole) 25°C | $\Delta\bar{S}^\circ$ (e.u.) | $\Delta\bar{V}^\circ$ (ml/mole) 15°C | 25°C | 40°C |
|---|---|---|---|---|---|---|
| 1 | 5.02 | −0.43 | −18 | −10.8 | −6.8 | −4.5 |
| 500 | 4.95 | −1.16 | −21 | − 9.8 | −.61 | −4.5 |
| 1,000 | 4.89 | −1.81 | −22 | − 7.6 | −5.7 | −4.5 |
| 1,500 | 4.80 | −2.07 | −23 | − 6.7 | −5.0 | −4.5 |
| 2,000 | 4.76 | −2.53 | −24 | − 3.1 | −3.9 | −4.5 |
| 2,500 | 4.71 | −2.67 | −25 | − 2.8 | −3.2 | −1.7 |
| 3,000 | 4.67 | −3.14 | −26 | − 1.8 | −2.6 | 0.0 |
| 3,500 | 4.65 | −3.05 | −26 | − 0.1 | −2.1 | +1.0 |
| 4,000 | 4.64 | −3.10 | −26 | − 0.1 | −1.7 | +1.0 |
| 4,500 | 4.61 | −2.93 | −25 | | −1.5 | |
| 5,000 | 4.59 | −3.80 | −28 | | −1.2 | |

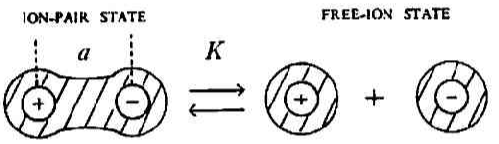


Fig. 3 A scheme of the equilibrium between an ion-pair and free ions

Using the following three theoretical equations for the dissociation constant of an ion-pair and the calculated average values of log $K$, the closest-approach distances of the ion-pair $\mathring{a}$'s are obtained at high pressures. From the Denison-Ramsey[2] equation,

$$K = \exp(-b), \tag{17}$$

$$b = \frac{|z_+z_-|e^2}{a_{D-R}DkT}, \tag{18}$$

where $a_{D-R}$, $e$ and $k$ are the closest-approach distance of the ion-pair in its model of Denison-Ramsey, the absolute electronic charge and Boltzmann's constant, respectively,

$$\mathring{a}_{D-R} = -\frac{4.354\times10^5}{DT\log K}\ (\text{Å}). \tag{19}$$

From the Fouss equation[3],

$$K = \frac{3000}{4\pi N a_F^3}\exp(-b), \tag{20}$$

where $a_F$ and $N$ are the closest-approach distance of the ion-pair in its model of Fuoss and Avogadro's number, respectively,

$$\log K = -3\log \mathring{a}_F + 2.5981 - 4.353\times10^5/(DT\,\mathring{a}_F), \tag{21}$$

which can be solved with respect to $\mathring{a}_F$ by successive approximation. From the Bjerrum equation[4],

$$K^{-1} = \frac{4\pi N}{1000}(ab)^3 Q(b), \tag{22}$$

where

$$Q(b) = \int_2^b x^{-4}\exp(x)\,dx, \tag{23}$$

$$\log Q(b) = -15.8831 - \log K + 3\log DT, \tag{24}$$

from which $Q(b)$ is calculated. Then, if $b$ is known from the table[15)20)] of the relation between $Q(b)$ and $b$ in eq. (23),

$$b = |z_+ \cdot z_-| e^2 / (a_B DkT) = 1.003 \times 10^6 / (\mathring{a}_B DT), \quad (25)$$

that is,

$$\mathring{a}_B = 1.003 \times 10^6 / (b DT). \quad (26)$$

The calculated values of $\mathring{a}_{D-R}$, $\mathring{a}_F$ and $\mathring{a}_B$ at high pressures at each temperature are plotted against pressure in Fig. 4.

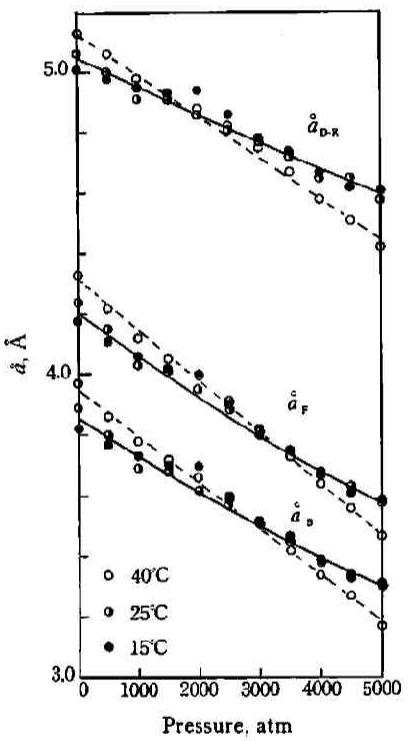


Fig. 4 The dependence of the closest-approach distances on pressure

As shown in Fig. 4, the closest-approach distances, $\mathring{a}_{D-R}$, $\mathring{a}_F$ and $\mathring{a}_B$, all decrease almost linearly with increasing pressure at each temperature. If the distance between the cation and the anion in the ion-pair decreases, the Coulombic interaction between them increases as the result of the stabilization of the ion-pair state. Perhaps, this is the reason why there appears a plateau in the curve of log $K$ *vs* pressure above 2,500 atm. If the ion-pairs are directly contact ones, the closest-approach distance would not be changed so much by pressure as shown in this experiment. So, this ion-pair $Co(NH_3)_6^{3+} \cdot SO_4^{2-}$ in water seems to be solvent separated one as mentioned above. Though all of the closest-approach distances, which have different definitions in each model, have smaller values than the sum of the crystal radii of the cation and the anion, they would become considerably larger, if

20) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths Scientific Publications, London (1965)

the bulk dielectric constant of water is replaced by a smaller effective dielectric constant paying regard to the dielectric saturation near ions.

Table 5 Changes in the closest-approach distances and the volume of the bulk water by pressure at 25°C

| $P$, atm | $(v^{(P)}/v^{(1)})^{1/3}$, | $d_{D-R}^{(P)}/d_{D-R}^{(1)}$, | $d_F^{(P)}/d_F^{(1)}$, | $d_R^{(P)}/d_R^{(1)}$ |
|---|---|---|---|---|
| 1 | 1.000 | 1.000 | 1.000 | 1.000 |
| 500 | 0.993 | 0.988 | 0.979 | 0.977 |
| 1,000 | 0.986 | 0.970 | 0.950 | 0.949 |
| 1,500 | 0.981 | 0.970 | 0.946 | 0.949 |
| 2,000 | 0.976 | 0.960 | 0.932 | 0.931 |
| 2,500 | 0.971 | 0.951 | 0.915 | 0.918 |
| 3,000 | 0.967 | 0.943 | 0.901 | 0.905 |
| 3,500 | 0.963 | 0.933 | 0.884 | 0.887 |
| 4,000 | 0.959 | 0.919 | 0.866 | 0.869 |
| 4,500 | 0.956 | 0.919 | 0.856 | 0.859 |
| 5,000 | 0.953 | 0.905 | 0.844 | 0.848 |

Furthermore, as shown in Table 5, the ion-pair is apparently more compressible than the bulk water, perhaps because the attractive force between paired ions promotes the decrease in $d$'s, in addition to the contraction due to the external pressure.

*Laboratory of Physical Chemistry*
*Department of Chemistry*
*Faculty of Science*
*Kyoto University*
*Kyoto, Japan*